Anal. Calcd. for $KAsF_6$: As, 32.8; F^-, 50.0; total AsF_6^-, 82.9. Found: As, 32.2 ± 0.6; $F^- = 48.8 \pm 0.5$; AsF_6, 82.7 ± 0.5; density $KAsF_6$, 3.29 g./ml.

The X-ray crystallography of $KAsF_6$ has been described by Roof.[13]

3. The Preparation of Ammonium Hexafluoroarsenate.—Two and three-tenths grams of arsenic pentoxide and 13.2 g. of ammonium fluoride were mixed well and fused in a nickel crucible. The ammonium hexafluoroarsenate crystallized from the melt. The product so obtained was contaminated with uncomplexed pentavalent arsenic and nickel salts. The crude material was purified by dissolving it in water and precipitating out all uncomplexed pentavalent arsenic as silver arsenate (silver hexafluoroarsenate is extremely water soluble). The excess silver from the precipitant was removed by adding a small quantity of ammonium chloride solution to the system. A small yield of relatively pure NH_4AsF_6 was obtained by evaporating this solution to near dryness and filtering off the crystals of the product. The material was dried at 110° and analyzed for AsF_6^-; AsF_6^- found, 91.5%; theory, 91.3%.

An adaptation of the procedure described by Palmer[14] for preparing NH_4PF_6 from KPF_6 and $[Cd(NH_3)_6](PF_6)_2$ gave a better synthesis of NH_4AsF_6 than the direct method described above.

4. Preparation of Hexafluoroarsenic Acid.—A solution of $KAsF_6$ was shaken with batches of Dowex-50 ion-exchange resin, in the acid form. The resulting solution of $HAsF_6$ was evaporated under reduced pressure. Eventually large colorless hexagonal crystals came out of solution. These crystals melted around room temperature and an AsF_6^- analysis indicated a composition corresponding approximately to the hexahydrate, $HAsF_6 \cdot 6H_2O$; AsF_6^- found, 65.1%; theory, 63.4%. The phosphorus analog has been reported by Lange.[15]

5. Preparation of Cesium Hexafluoroarsenate.—Impure cesium hexafluoroarsenate was prepared by mixing solutions of $KAsF_6$ and commercial cesium chloride; the cesium salt immediately precipitated. A low analysis for AsF_6^- (observed, 52.5%; theory for $CsAsF_6$, 58.7) was traced to impurities in the product. $2Na_3AsO_4 \cdot NaF \cdot 19H_2O$ and Cs_2SiF_6 were identified as contaminants by Dr. C. E. Nordman using crystallographic methods. More detailed crystallographic data on the cesium and ammonium salts have been collected by Dr. Nordman and will be available in another publication.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CITY COLLEGE OF NEW YORK]

The Mechanism of the Precipitation of Magnesium Oxalate from Supersaturated Solutions. II. The Heat and Entropy of Activation[1]

BY BERNARD LICHSTEIN[2,3] AND FRANK BRESCIA

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The heat and entropy of activation and the entropy change for the over-all reaction have been obtained for the precipitation of magnesium oxalate from its supersaturated solution. The rate of nucleation also has been estimated. The results are interpreted in terms of the previously proposed mechanism.

Introduction

In our previous paper,[4] it was stated that, on the basis of the proposed mechanism of the precipitation of magnesium oxalate from supersaturated solutions, the entropy of activation and the entropy change for the over-all reaction would be of the same order of magnitude. Measurements of the temperature dependence of the rate constant for the precipitation of magnesium oxalate and of the solubility of magnesium oxalate have therefore been made.

The experimental procedures used are essentially the same as previously recorded.[4]

The heat and entropy of activation were calculated from

$$\Delta H^* = \frac{2.30RT_1T_2}{T_2 - T_1} \log \frac{k_2}{k_1}$$

and

$$\Delta S^* = 2.30R \log \frac{kNh}{\kappa RT} + \frac{\Delta H^*}{T}$$

making the usual assumption that $\kappa = 1$. The numerical value of the equilibrium constant, K, at zero strength, for the over-all reaction

$$MgC_2O_4 \cdot 2H_2O \text{ (solid)} = Mg^{++} + C_2O_4^{--} \text{ (aqueous soln.)}$$

was calculated from $K = C^2_{C_2O_4^{--}} \cdot \gamma^2_{MgC_2O_4}$, in which $C_{C_2O_4^{--}}$ refers to the concentration of oxalate in moles per liter in a saturated solution of magnesium oxalate. The solubility was measured as a function of ionic strength and the results were extrapolated to $\mu = 0$, at which condition $\gamma = 1$.

The standard thermodynamic quantities $\Delta F°$, $\Delta H°$ and $\Delta S°$, for the over-all reaction as written above, were calculated from the usual equations

$$\Delta F° = -2.30RT \log K$$

$$\Delta H° = \frac{2.30RT_1T_2}{T_2 - T_1} \log \frac{K_2}{K_1}$$

$$\Delta S° = \frac{\Delta H° - \Delta F°}{T}$$

The results are summarized in Table I. The redetermined rate constant at 25.0° agrees within

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[2] The research was carried out while a senior at The City College of New York.

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2% with the previously determined value.[4] The ratio of the equilibrium constant at 35° to that at 25°, 1.11, is in excellent agreement with the value, 1.12, calculated from the calorimetrically measured heat of solution of magnesium oxalate in 3.8 *M* hydrochloric acid solution.[5]

TABLE I

Constant ionic strength = 0.938; constant *p*H = 5.70

Kinetic data for the crystal growth reaction				Equilibrium data for the over-all reaction $MgC_2O_4.2H_2O(solid) = Mg^{2+} + C_2O_4^- + 2H_2O$			
Temp., °C.	$k \times 10^3$, min.$^{-1}$	ΔH^*, cal./mole	ΔS^*, cal./mole-deg.	$K \times 10^6$	$\Delta F°$, cal./mole	$\Delta H°$, cal./mole	$\Delta S°$, cal./mole-deg.
25.0	3.35			5.08	7219		
		2978	−68.1			1820	−18.1
35.1	3.96			5.62	7402		

Discussion

The observed heat of activation is only about 3 kcal. per mole, indicating that the growth of the individual nuclei is controlled by the rate of diffusion of magnesium oxalate molecules. This result is consistent with the proposed mechanism and is substantiated by the study of the effect of stirring on the precipitation rate. The rate of a reaction in a condensed phase, controlled by the diffusion of molecules to the reaction sites rather than by the actual chemical change, should increase with stirring. An appreciable stirring effect has been found.[6] The plot of log ml. Ce^{4+} *vs.* time, after precipitation starts, yields a straight line only for a comparatively short period of time after which the ml. Ce^{4+} decreases much more rapidly than in the absence of stirring.

Further confirmation of our mechanism and of the conclusion that the rate is diffusion controlled is obtained from the following calculation of the rate of nucleation. The application of the theory of absolute rates to the Volmer–Becker theory of nucleation leads[7] to the following approximate expression for the absolute rate of nucleation in condensed systems in which r is the rate, in nuclei

$$r \cong \frac{NkT}{h} \exp[-(\Delta f^* + \Delta F^*)/kT]$$

formed per mole per sec., to an order of magnitude. Δf^* is the free energy of activation for the growth rate, based on the assumption that a short range diffusion of molecules is involved. ΔF^* is the maximum free energy necessary for the nucleus formation process. Subcritical nuclei or embryos require free energy for further growth while the nuclei grow freely with decreasing free energy. k in this equation is the Boltzman constant and the other symbols possess their usual meaning. An estimation of ΔF^* is given[8] in the terms

$$\Delta F^* = An^{*2/3} - Bn^*$$

in which

$$An^{*2/3} = 4\pi\left[\frac{\Delta H}{12N}\right]\left[\frac{3n^*}{4\pi}\right]^{2/3}$$

and

$$Bn^* = n^*kT \log S_2/S_1$$

n^* is the number of molecules in the critical nucleus,[4] 2. ΔH is the heat of solution, 7.62×10^{10} ergs per mole, from Table I. S_2/S_1 is the ratio of the concentration of magnesium oxalate in the supersaturated solution to the concentration of the saturated solution at the same temperature,[4] 180. Using these values, ΔF^* is calculated to be -1.05×10^{-13} ergs per nucleus. Δf^*, from Table I, is 9.74×10^{11} ergs per mole at 298°K. From these free energy changes, the rate of nucleation is calculated to be 4×10^{20} nuclei per mole per sec. Thus, the critical nuclei are rapidly and completely formed and, thereafter, the growth rate is independent of the number of nuclei.

Although the heat of activation is comparatively small, the rate of growth of the individual nuclei is largely controlled by the entropy of activation. The entropy contribution, −68 cal. per mole per deg., makes the entropy factor unusually small producing a significant depressing effect on the rate. The entropy of formation of the magnesium oxalate from its ions in solution, on the other hand, is also fairly large but positive, +18.1 cal. per mole per deg. These results may be interpreted as follows.

The heat of solution of magnesium oxalate is comparatively small, about 1.8 kcal. per mole. But the heat of hydration of magnesium ion, estimated from the Born equation,[9] using 6.5×10^{-9} cm. for the radius of the magnesium ion,[10] is of the order of magnitude of 10^3 kcal. per mole. Thus, as expected because of its charge and comparatively small size, the magnesium ion is a highly hydrated ion. The hydration of oxalate ion is probably negligible. Thus, in the initial state, the magnesium ion is strongly bound to water molecules; in the final crystalline state, the ion is largely dehydrated and therefore less restrained. This accounts for the observed increase in entropy accompanying the formation of solid magnesium oxalate from its ions.

The decrease in entropy accompanying the formation of the activated complex in the reaction nuclei + MgC_2O_4 means the complex is not readily formed. Thus, it may be imagined that, after the MgC_2O_4 molecule diffuses to the surface of a nucleus, complex formation must involve a rearrangement of the molecule into a highly hydrated quasi ionic state.

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